(12) **UK Patent** (19) **GB** (11) **2 178 746** (13) **B**

(54) Title of Invention

Clouded plastics elements

(51) INT CL⁴; C08L 33/04 // G03B 21/56

(21) Application No
8619183

(22) Date of filing
6 Aug 1986

(30) Priority data

(31) 3528165

(32) 6 Aug 1985

(33) Fed. Rep. of Germany
(DE)

(43) Application published
18 Feb 1987

(45) Patent published
1 Feb 1989

(52) Domestic classification
(Edition J)
C3M 107 136 145 146 152
153 155 165 300 C
U1S 2226 3038 3069 3070
3073 C3M

(56) Documents cited
GB 1370785
US 4464513

(58) Field of search
C3M
C3V

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Clouded plastics elements

The present invention relates to clouded plastics
elements. More particularly it relates to shaped
and flat plastics elements comprising inherently
transparent plastics which are particularly suitable
5 as light projection screens e.g. as television
projection screens.

Various technical tasks can only be performed by
using partly transparent glass. These tasks include
10 the job of making glass matt and the manufacture
of projection screens and other optical display
elements.

As a rule, use is made of light refraction or light
15 scattering at phase limits, such as occurs, for
example, when particles of suitable dimensions
are embedded as a dispersed phase in a carrier
phase and the two phases have different refractive
indices. The carrier phase advantageously consists
20 of for example, plastics. Manufacturers active
in this field have developed, as well as inorganic
particles such as glass beads, polymer particles
suitable for embedding in the carrier phase.

25 Thus, for example, DE-A-21 46 628 discloses a
method of polymerisation for preparing finely divided
polymer particles, in which a monomer system (A)
is prepared, which is capable of free radical addition
polymerisation and which contains

30

87 to 99.99% by weight of a monoethylenically unsaturated
                            monomer and
0.01 to 3% by weight   of at least one polyunsaturated
                            monomer, and

5 to 50% by weight,   based on the total mixture,
of a different soluble thermo-
plastic addition polymer
is totally dissolved in
5   the monomer system (A),
the first polymer being
insoluble in the thermoplastic
polymer; and

the solution of the two is subjected to conditions
10 under which the monomer system undergoes free radical
polymerisation forming substantially spherical
cross-linked polymer particles, having an average
particle size in the range from 0.5 to 30 microns,
these particles being dispersed in a continuous
15 phase of the thermoplastic polymer.

The polymer particles which are formed according
to DE-A-21 46 628 are cross-linked and are therefore
scarcely capable of fusion and deformation, with
20 the result that they can be compressed with powders,
for example, or subjected to injection moulding.

In the form of a solution, the polymer formed according
to this citation may, for example, be sprayed onto
25 acrylic resin sheets. The citation mentions the
possibility of using the polymer as a dulling lacquer
and in the form of mixtures which are suitable
for the manufacture of optical screens with backwards
projection and in computers, in the television
30 and film industries, in photography, etc.

DE-A-21 46 607 also discloses translucent to opaque
plastics mixtures which contain spherical cross-
linked particles of addition polymer consisting
35 of 87-99.99% by weight of at least one monoethylenically
unsaturated monomer and 0.01 to 3% by weight of
a monomeric cross-linker dispersed in a continuous

phase of an addition polymer, the addition polymer
being soluble in the mixed monomers. The plastics
mixture preferably also contains additional copolymerised
cross-linking agent. Possible fields of application
5   mentioned in this citation are self-supporting
translucent plastics sheets, strips of film and
the like. When a solution of the polymeric material
is sprayed onto acrylic films, matt films are obtained.
The mixtures are also supposed to be suitable for
10   image screens with backward projection.

JP-A-80 93102 (Chem. Abstr. 93, 240792y) describes
light-scattering acrylic resin sheets which are
obtained by belt polymerisation from acrylic resin
15   film and acrylate monomers which contain a light-
scattering agent in sandwich configuration.

JP-A-81 117 225 (Chem. Abstr. 96, 86627b) discloses
optical screens which have a broad light diffusing
20   effect in one direction and act as optical lenses
in the other direction. The screens according
to JP-A-81 117 225 are produced by embedding powdered
glass fibres in modified acrylic resin and subsequently
carrying out monoaxial stretching, followed by
25   a final coating with an acrylate layer containing
carbon black. Light-scattering acrylic resin sheets
used as projection screens are the subject of JP-A-
82 05742 (Chem. Abstr. 96, 200768a), in which
the desired light scattering is achieved by means
30   of quartz pellets 0.5 to 20 microns in diameter
embedded in PMMA (polymethylmethacrylate). According
to British Patent 1 585 338, light-scattering sheets
with better optical resolution, greater optical
half-power angles and greater flexibility than
35   conventional sheets containing glass fibres are
obtained by using plastics sheets filled with glass
beads. The glass beads have diameters of from

0.001 to 0.05 mm. Examples of carrier materials
mentioned are thermoplastics such as cellulose
esters, polycarbonate, polyarylsulphone, polystyrene
and acrylic resins.

5 The solutions in the prior art concerning "translucent
to opaque plastics mixtures and the use thereof,
for example, in the manufacture of sheet or film
material" have not proved entirely satisfactory.
In particular, requirements have not been fully
10 met with regard to suitability as optical projection
screens. It was also desirable that the material
should be extrudable without any serious technical
disadvantages.

We have now found that certain clouded, particularly
15 shaped flat plastics elements satisfy the demands
made of optical projection screens, especially
television projection screens, to an exceptional
degree if cross-linked bead-polymerised beads are
incorporated into a polymer matrix (PM) in an amount of from
20 1 to 30% by weight, based on the polymer matrix (PM), these
cross-linked beads being formed of polymer P which comprises

9.9 to 59.9% by weight of one or more radically
polymerisable monomers A
which contain an aromatic
25 group or non-aromatic monomers
A' which contain halogen,
and
90 to 40% by weight of vinyl monomers B which
are copolymerisable with
30 said monomers A and A' but
different from them, and
0.1 to 20% by weight of at least one cross-linking
monomer V,

with the proviso that

a)   the refractive index of the polymer P is
     higher than that of the polymer matrix and

b)   the average bead size of the beads is 5
     to 50 microns, preferably 10 to 35 microns.

Polymer P may also contain from 0 to 10% by weight
of a (strongly) polar monomer H.

Examples of radically polymerisable monomers A
which contain an aromatic group are monomers of
formula I

$$Ar - \left[(O)_m - R'_p - O - \overset{O}{\underset{"}{C}} - \right]_n \overset{R}{\underset{|}{-C}} = CH_2 \qquad I$$
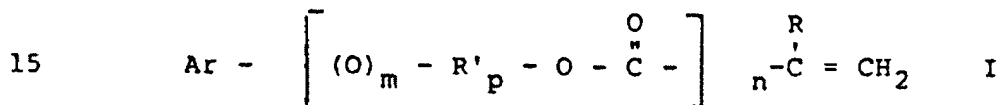
wherein Ar represents an optionally substituted
aromatic hydrocarbon group with up to 12 carbon
atoms, preferably an aromatic group optionally
substituted with C_{1-4} alkyl groups or with fluorine,
chlorine or bromine or both types of substituent,
more particularly a phenyl group,

R   represents hydrogen or methyl,
R'   represents an optionally branched alkylene
      group with 1 to 8 carbon atoms,
n   represents zero or one,
m   represents zero or one, and
p   represents zero or one, with the proviso
      that if p represents zero, m must also represent
      zero.

Homo- and copolymers formed solely from monomers
of formula I generally have a refractive index
N_d of more than 1.56.

Preferably, the monomers of formula I are styrene
and/or the methyl-substituted derivatives thereof
such as α-methylstyrene and p-methylstyrene, p-

ethylstyrene and halogenated derivatives of styrene
such as p-chlorostyrene. Other examples of monomers
A of formula I include phenylacrylate and -methacrylate,
xylylenemethacrylate and -acrylate, particularly
5 the m-form, 4-methylphenylacrylate and -methacrylate,
2-phenylethylacrylate and -methacrylate, 3-phenyl-
1-propylmethacrylate and -acrylate, and 2-phenyloxyethyl-
acrylate and -methacrylate.

10 Of the non-aromatic monomers A' which contain halogen,
preferred are those which contain, in particular,
chlorine or bromine in a non-activated and therefore
readily hydrolysable bond, for example the α-chloro-
and α-bromoacrylic and -methacrylic acid esters
15 of C_{1-6} alcohols such as methyl-α-chloroacrylate
and also vinyl chloride and vinylidene chloride.

Of the copolymerisable vinyl monomers B, preferred
are those of formula .II
20

$$CH = \overset{\overset{\displaystyle R}{\displaystyle |}}{C} - COOR" \qquad II$$

wherein R represents hydrogen or methyl and R"
25 represents an optionally branched, optionally cyclic
alkyl group with 1 to 8 carbon atoms, whilst the
cyclic alkyl groups preferably have at least 5
cyclic carbon atoms. Various examples of monomers
of groups A, B and C may be used provided that
30 their activity corresponds to the features specified.
Homo- and copolymers formed solely from monomers
of formula II generally have a refractive index
.N_d of < 1.51, generally less than 1.49.

35 The vinyl monomers B are preferably chosen so that
the resulting glass temperature T_g (measured by
dilatometry) of a polymer or copolymer prepared

therefrom would be at least 80°C. (For the T_g and the contributions of the monomers, see Brandrup-Immergut and B. Vieweg, F. Esser, in the Plastics Handbook, Volume IX, Hanser-Verlag 1975, pages
5 333 to 340; T.G. Fox Bull. Am. Phys. Soc. 1, 125, 1956).

It is particularly preferred that the vinyl monomer B should consist either wholly or to an extent
10 of at least 40% by weight of methylmethacrylate.

Of the cross-linking monomers V, preferred are the known radical cross-linkers. The cross-linking monomers usually have more than one radically polymerisable
15 unit in the molecule. Mention should be made of those with two vinyl groups such as divinylbenzene, also acrylic and methacrylic acid esters and amides of polyols such as glycoldi(meth)acrylate, 1,3- and 1,4-butanediol(meth)acrylate, trimethylolpropanetri-
20 (meth)acrylate, tetraethyleneglycoldi(meth)acrylate, and so on, and also monomers which contain vinylidene, the (hidden) amide methylol, carbamide methylolether, azlactone and epoxy groups, such as N-methylol(meth)-acrylamide, methylenebisacrylamide and -methacrylamide,
25 glycidyl(meth)acrylate, and particularly also cross-linking monomers with unsaturated groups of graduated reactivity in the molecule such as the vinyl, allyl and crotylesters of acrylic and/or methacrylic acid. (Cf. H. Rauch-Puntigam, Th. Völker, Acrylic
30 and Methacrylic Compounds, Springer-Verlag Berlin, 1967).

Cross-linking is intended to ensure that the beads do not fuse during processing at elevated temperature
35 (up to about 300°C).

Bead polymers may be prepared in known manner by

the process of bead polymerisation. In this process,
monomers A, B and V, as a dispersed phase, are
generally distributed by mechanical force (agitation)
in a non-solvent (continuous phase) and polymerised
5   in this form. The polymer formed is predominantly
soluble in the monomer. Under the effect of interfacial
tension the monomer forms spherical drops. In
order to obtain this droplet shape during polymerisation
and prevent the drops from running together, so-
10   called "dispersers" or distributors (protective
colloids) are added to the polymerisation mixture,
preferably substances which can be totally removed
from the bead polymer after polymerisation is complete.

15   The "distributor" ensures that, once formed, the
droplets of monomer are stabilised so that it is
virtually impossible for the drops to join together.

Water is generally used as the continuous phase.
20   Therefore, primarily sparingly soluble to water-
insoluble radically polymerisable monomers are
used as the monomers suitable for polymerisation.
(Cf. Houben-Weyl, 4th Edition, Volume XIV/1 "Macromolecular
substances", pages 406 to 433, G. Thieme-Verlag
25   1961).

Suitable distributors include (water-insoluble)
salts of inorganic acids such as barium sulphate
or barium carbonate or high molecular natural substances
30   or synthetic polymers. The group of high molecular
distributors includes water-soluble colloids such
as polyvinyl alcohol, partially saponified polyvinylacetate,
methylcellulose, starch, gelatine, pectin, the
alkali metal salts of polyacrylic acid or the alkali
35   metal salts of styrene or vinylacetate-maleic anhydride
copolymers and the like (cf. Houben-Weyl, loc.cit,
page 411 - 430). The ratio of aqueous to monomeric

phase is generally from 2:1 to 4:1. In bead poly-
merisation, as is well known, starters are used
which are, in a first approximation, soluble in
the monomer but insoluble in water. As a rule,

5   the quantity of starter used is from 0.1 to 1%
by weight, preferably around 0.5% by weight based
on the monomers. Suitable starters include the
conventional organic peroxides or corresponding
azo compounds which are soluble in the monomer,

10   such as dibenzoylperoxide, lauroylperoxide and
azoisobutyronitrile. Radical forming agents with
fairly high temperatures of decomposition may addi-
tionally be used if the temperature is increased
towards the end of the reaction in order to achieve

15   the maximum possible polymerisation. The bead
size can be adjusted between 5 and 50 microns within
the scope claimed.

Moreover, if desired, regulators such as the conven-
tional sulphur regulators, e.g. aliphatic mercaptans

20   such as laurylmercaptan and tert.dodecylmercaptan
may be added to the bead polymerisation mixture.
The average molecular weight M_w of the polymer
P according to the invention if it were not cross-
linked would generally be in the range from 1 to

25   2.10^5 g/mol; a figure of about 10^5 g/mol should
be taken as an approximate value (M_w determined
by gel permeation chromatography).

It is also possible to add conventional lubricants
such as fatty alcohols, stearic acid esters, palmitic

30   acid esters or natural waxes, preferably before
polymerisation.

A practical method of preparation may consist of
first putting in the water, the monomers A, B and
V, the starter dispersant and optionally lubricant

and then heating the mixture, for example to about
90°C. If necessary, the excess heat of polymerisation,
particularly upwards of 95°C, is removed by external
cooling.

5   The temperature will generally not exceed 115°C.
The duration of polymerisation is usually in the
range from 1 to 5 hours. The viscosity of the
polymerisation mixture (measured with a Brookfield
Viscosimeter) is generally in the range between
10 8000 and 800 Centipoise.

The partly reactive lubricants are preferably only
added after about 20% conversion. Regulators may
also be added in the course of polymerisation.

After the end of the reaction the beads are generally
15 separated off by filtering or centrifuging. Any
additives adhering to them can be eliminated by
any suitable means, for example by washing with
dilute acid and water. The beads are frequently
dried with heating, preferably with air circulating
20 round them, e.g. in rack dryers.

The polymer matrix PM to which the pearls are added
is generally a transparent, usually thermoplastic
synthetic material such as those which have already
caught on in the art for the purpose of light projection.

25 The ratio of P to PM is most desirably determined,
inter alia, by the fact that the difference between
the refractive indices n_D (beads) minus n_D (polymer
matrix) should be at least 0.01, preferably 0.04.

Suitable plastics for the polymer matrix include
30 polystyrenes, PVC, polyvinylacetate, polycarbonate,
polyolefins and, in particular, acrylic resins.

The term "acrylic resins" within the scope of this
invention refers to polymers which are made up
of at least 50% by weight of monomeric esters of
acrylic and/or methacrylic acid, particularly of
5 the same type as formula II.

In order to prepare the clouded plastics elements
according to the invention, the beads consisting
of the polymer B must be incorporated in the polymer
matrix and then distributed therein.

10 It is particularly surprising that we have succeeded
in introducing the beads in the course of processing
the polymer matrix PM with the aid of extruders.
The beads are added to the extruder melt.

It was unexpected that a) the beads would retain
15 their shape under the temperature and shearing
conditions of extrusion and b) it would be possible
to achieve the homogeneous distribution of the
beads which is absolutely essential for the desired
light scattering effect. Moreover, surprisingly,
20 the jump in refractive indices at the interfaces
between the polymer matrix PM and the polymer beads,
which was also necessary to give the required light
scattering effect, was achieved. There was a danger
that this jump in the pattern of the refractive
25 index at the above-mentioned interfaces would be
"evened out" by diffusion processes - as occurs,
for example, when the beads are introduced into
polymerisable monomers - which would result in
an undesirable change in the scattering effect.

The invention will be illustrated by the following
non-limiting examples:

5 Example 1: Bead Polymerisation:

In a 1001 vessel made of V4A steel and equipped
with a nitrogen inlet and an Impeller stirrer 600g
of $Al_2(SO_4)_3 \cdot 18H_2O$ and 6g of sodium paraffin sulfonate
(trade mark STATEXAN of Bayer, Leverkusen) are
10 disolved in 501 of deionised water at 85°c and
with stirring at 350rpm. The aluminium compound
used as dispersant is precipitaed by adding 264g
of sodium carbonate. Susequently a monomer mixture
of 5.9kg of methylmethacrylate, 4.0kg of styrene,
15 0.1kg of glycol dimethacrylate and 0.2kg of dilauroyl
peroxide is added under nitrogen. Polymerisation
is carried out at 80°c for 140 minutes and subsequently
at 90°c for 60 minutes with continued stirring.

After cooling to 50°c the polymerisation mixture
20 is treated with 600ml of sulphuric acid (50%) to
dissolve the dispersant. The bead material is
collected on a filter funnel, washed with deionised
water and dried on hurdles for 20 hours at 50°c.
The average size of the beads (medium value) thus
25 produced is 37 microns and the refractive index
of the beads is found to be 1.53.

Example 2: Production of Light Dispersing Plates
by Extrusion:

30 (see Kirk-othmer, 3rd. ed. Vol 18, pages 185-190,
ibid, Vol 15, pages 632-637).

In a twin cone-and-screw mixer 96.5 parts by weight
of polymethylmethacrylate (PMMA) moulding material

(trade mark PLEXIGLAS 7N of Röhm GmbH) are mixed,
optionally with the addition of adhesion promoters
as conventionally used in the art. The mixture
is extruded in a single screw extruder with degassing

5   at a material temperature of 245°c to yield plates
3mm thick. These plates meet fully the requirements
with regard to light dispersion and mechanical
properties.

Alternatively, the beads may be added to the extruder

melt with excellent results.

Transmission (= ratio of transmitted brightness to

incident illumination) = 87-89%.

Half brightness angle (angle at which brightness is

one half of maximum transmitted brightness) = 8+/-

1.5°.

Claims

1.   Clouded plastics elements which comprise
a polymer matrix (PM) into which cross-linked
bead-polymerised beads in an amount of from 1 to 30%
by weight, based on the polymer matrix (PM), have
been incorporated, said cross-linked beads being formed
5 of polymer P which comprises

9.9 to 59.9% by weight of one or more radically
                         polymerisable monomers A
                         which contain an aromatic
                         group or non-aromatic monomers
10   A' which contain halogen
                         and
90 to 40% by weight   of vinyl monomers B which
                         are copolymerisable with
                             monomers A and A' but
15   are different from them
                         and
0.1 to 20% by weight   of at least one cross-linking
                         monomer V,

with the proviso that

20 a)   the refractive index of the polymer P is
         higher than that of the polymer matrix (PM)
         and that

    b)   the average bead size of the beads is 5 to
         50 microns.

25 2.   Clouded plastics elements as claimed in claim
    1 wherein polymer P includes from 0 to 10% of a
    polar monomer H.

    3.   Clouded plastics elements as claimed in claim

1 or claim 2 wherein the average bead size of the
beads is 10 to 35 microns.

4.   Clouded plastics elements as claimed in any
of claims 1 to 3 wherein the radically polymerisable
5 monomers A which contain an aromatic group are
monomers of formula I

$$Ar - \left[(O)_m - R'_p - O - \overset{O}{\overset{\|}{C}} - \right]_n \overset{R}{\overset{|}{-C}} = CH_2 \qquad I$$
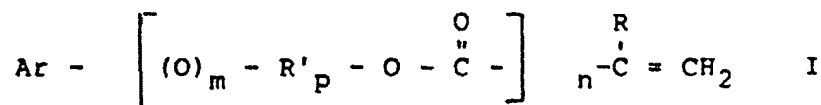
wherein Ar represents an optonally substituted aromatic
hydrocarbon group with up to 12 carbon atoms,
10 R   represents hydrogen or methyl,
    R'   represents an optionally branched alkylene
            group with 1 to 8 carbon atoms,
    n   represents zero or one,
    m   represents zero or one, and
15 p   represents zero or one, with the proviso
            that if p represents zero, m must also represent
            zero.

5.   Clouded plastics elements as claimed in any
one of claims 1 to 4 wherein

20 Ar represents an aromatic group optionally substituted
with C_{1-4} alkyl groups or with fluorine, chlorine
or bromine or both types of substituent, more particularly
a phenyl group,

and R, R', n, m and p are as defined in claim 4.

25 6.   Clouded plastics elements as claimed in any
one of claims 1 to 5 wherein the monomers of formula
I (as defined in claim 4) are styrene and/or the
methyl-substituted derivatives thereof.

7.   Clouded plastics elements as claimed in any
one of claims 1 to 6 wherein the copolymerisable
vinyl monomers B are those of formula II

$$CH = \overset{\overset{\textstyle R}{|}}{C} - COOR'' \qquad\qquad II$$

5   wherein R represents hydrogen or methyl and R"
represents an optionally branched, optionally cyclic
alkyl group with 1 to 8 carbon atoms, whilst the
cyclic alkyl groups preferably have at least 5
cyclic carbon atoms.

10 8.   Clouded plastics elements as claimed in any
one of claims 1 to 7 which are produced by adding
the cross-linked beads in metered amounts to the
melt of the polymer matrix PM in the course of
an extrusion process.

15 9.   Clouded plastics elements as claimed in claim
1 substantially as herein described.

10.   A process for the preparation of clouded plastics
elements as defined in claim 1 comprising incorporating
beads produced by bead polymerisation in aqueous
20 media and isolated therefrom into said polymer matrix.

11.   A process as claimed in claim 10 wherein said
beads produced by bead polymerisation in aqueous
media and isolated therefrom are incorporated into
said polymer matrix in a molten state in an extruder
25 and said mixture is extruded.

12.   A process as claimed in claim 10 substantially
as herein described.